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(54) Title: METHOD FOR FRACTIONATION OF SUCROSE-CONTAINING SOLUTIONS

(57) Abstract

The invention relates to a method for separating sucrose and a second dissolved component from a beet-derived sucrose-containing solution, wherein the solution is subjected to a first fractionation by a chromatographic simulated moving bed method to yield a sucrose-enriched fraction and a fraction enriched with the second dissolved component, or a fraction enriched with sucrose and the second component, and the resulting fraction enriched with the second component or with sucrose and the second component is subjected to a second chromatographic fractionation, to yield a second sucrose-enriched fraction and a separate fraction enriched with the second dissolved component.

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Method for fractionation of sucrose-containing solutions

The present invention relates to a method for
separating sucrose and additionally a second dissolved
5   component from a solution. More particularly, the inven-
tion relates to a method in which a solution containing
sucrose and other dissolved substances is first frac-
tionated by a chromatographic simulated moving bed (SMB)
method to yield a sucrose-enriched fraction and a frac-
10   tion enriched with a second component to be recovered,
or a fraction enriched with sucrose and said second com-
ponent, and the fraction enriched with said second
component and optionally sucrose is further fractionated
chromatographically, either by a batch method or a
15   simulated moving bed method. In a preferred embodiment,
the invention relates to the fractionation of a beet-
derived sucrose-containing solution to yield a sucrose-
enriched fraction and a fraction enriched with a second
organic compound commonly present in beet-derived solu-
20   tions, such as betaine, inositol, raffinose, galactinol,
or serine and other amino acids.

The description hereinbelow employs the estab-
lished abbreviation SMB for the simulated moving bed,
which is customary in the art of chromatography.

25   It is known that sucrose and betaine are recov-
erable from molasses by chromatographic separation
methods. International published application WO
81/02420, which corresponds to Finnish Patent 77,845 to
Suomen Sokeri Oy, describes a chromatographic method for
30   the recovery of betaine from molasses by a batch process
in which diluted molasses is fractionated with a poly-
styrene sulphonate cation exchange resin in alkali metal
form. This method achieves good separation of sucrose
and betaine. This reference also discloses a method in
35   which a betaine-enriched fraction obtained from a first

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fractionation is subjected to further chromatographic
purification. The further purification step is capable
of separating the other components of the betaine-
enriched fraction. However, the dry solids content in
5   the sucrose and betaine fractions obtained by this
method is relatively low, therefore, large amounts of
eluant water must be evaporated in recovering the
sucrose and betaine from the respective fractions by
crystallization.

10   Continuously operated chromatographic separation
processes nowadays commonly employ the SMB method, which
method is used in a variety of different applications.
The SMB method has a separating performance that is
several times higher than that of the batch method, and
15   also results in significantly lower dilution of the
products or, conversely, lower consumption of eluant.

The SMB method may be carried out in either a
continuous or a sequential mode. In a continuous SMB
method, which was first disclosed in the early 1960s in
20   U.S. Patent 2,985,589, all fluid streams typically flow
continuously. These streams are: supply of feed solution
and eluant, recycling of liquid mixture, and withdrawal
of products. The flow rate for these flows may be
adjusted in accordance with the separation goals, i.e.
25   increased yield, purity, or capacity. Separation of
sucrose by such continuous SMB methods has been
described in international published application WO
91/08815 by The Amalgamated Sugar Company and in U.S.
Patent 4,990,259 to M. M. Kearney and M.W. Mumm and
30   assigned to The Amalgamated Sugar Company.

In a sequential SMB method, the pattern of fluid
streams is the same as in the continuous SMB method, but
some of the fluid streams do not flow continuously.
Sequential SMB fractionation methods in which a sucrose
35   fraction and a betaine fraction are recovered from beet

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molasses are disclosed in Finnish Patent 86,416 to
Suomen Sokeri Oy, which corresponds to U.S. Patent
5,127,957, and international published application WO
94/17213 to Suomen Sokeri Oy. German Offenlegungsschrift
5   4,041,414 to Japan Organo Co, which corresponds to
British published application 2,240,053, also discloses
a sequential SMB method by which several product frac-
tions are recovered from sugarbeet molasses.

In the sugar industry, the important parameters
10 in the fractionation of molasses to recover sucrose in-
clude the purity and yield of sucrose, the separation
capacity, and the eluant/feed ratio. A purity of 92% and
a yield of 90% are the usual requirements for a sugar
product. In order to increase the capacity, the flow
15 rates, which are generally higher in SMB processes than
in batch processes, are increased. Along with the in-
crease in the flow rate, however, a "flat tail" is pro-
duced in the sucrose elution profile. This is especially
disadvantageous when it is desired to recover, in addi-
20 tion to sucrose, a second dissolved component. With
respect of the recovery of sucrose and betaine, this
effect is apparent upon comparison of the elution pro-
files presented in international application WO 81/02420
and Finnish Patent 86,416, for example. In the course of
25 obtaining a high sucrose yield, the betaine yield is di-
minished because part of the betaine is allowed to pass
into the sucrose fraction wherefrom it is removed in the
sucrose crystallization step. Likewise, if a high beta-
ine yield is desired, considerable amounts of sucrose
30 end up in the betaine fraction, thus diminishing the
sucrose yield and considerably impairing the purity of
the betaine fraction.

In the above references, the purity of the beta-
ine fraction obtained by the process of German Offen-
35 legungsschrift 4,041,414 is relatively good, 80.9% on a

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dry solids basis (d.s.), but the purity of the sucrose
fraction, 87% d.s., is inadequate in view of the needs
of the sugar industry. It can be concluded from the com-
position of the feed solution of Example 3 in said
5   reference that the "thin juice" was demineralized prior
to the SMB fractionation by the "KAAK method" (which
refers to cation exchange - anion exchange - anion ex-
change - cation exchange as described in Sayama, K.,
Kamada, T., and Oikawa, S., *Production of Raffinose: A*
10   *New By-Product of the Beet Sugar Industry*, British Sugar
plc, Technical Conference, Eastbourne 1992). Molasses
produced by such a beet sugar process has a different
composition from common molasses. Typically, beet molas-
ses contains 1.5-3.5% by weight of raffinose and 3.5-
15   6.5% of betaine on a dry solids basis. On the other
hand, since the feed solution of Example 3 in German
Offenlegungsschrift 4,041,414 has a raffinose content of
17.3% by weight and a betaine content of 12.2% by weight
dry solids basis, it can be concluded, on the basis of
20   the raffinose-to-betaine ratio, that roughly half of the
betaine contained in common beet molasses was lost
(obviously in the ion exchange treatment).

        In accordance with the results presented in
Finnish Patent 86,416, a purity as high as 70.9% d.s.
25   for the betaine fraction was obtained (11.1% d.s. of
sucrose present). However, the 86.8% purity of the
sucrose fraction does not meet the requirements of the
sugar industry. Similarly, the 47.5% purity of the beta-
ine fraction reported in international application WO
30   94/17213 is rather poor.

        The object of the present invention is a fraction-
ation method by which sucrose and additionally a second
desired organic component, such as betaine, inositol,
raffinose, galactinol, or serine and other amino acids,
35   can be recovered from a beet-derived sucrose-containing

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solution so as to obtain higher yields and at least
equivalent purity for sucrose.

It is another object of the present invention to
fractionate sucrose and betaine so as to obtain higher
5   yields and/or higher purity for the second recovered com-
ponent, specifically betaine, as compared with the res-
ults obtained by the prior SMB methods.

It is a further object of the invention to pro-
vide an economical fractionation in terms of capacity
10   and the eluant/feed ratio - at least equivalent to the
prior SMB methods for fractionating sucrose-containing
solutions.

These objects are achieved with the method of the
invention for separating sucrose and additionally a
15   second dissolved component from a sucrose-containing
solution, in which method the solution is subjected to a
first chromatographic fractionation by a SMB method to
yield a sucrose-enriched fraction (hereinafter the first
sucrose fraction) and a fraction enriched with the
20   second dissolved component, and the resulting fraction
enriched with the second component is subjected to a
second chromatographic fractionation, to yield a second
sucrose-enriched fraction (hereinafter the second
sucrose fraction) and a separate fraction enriched with
25   the second dissolved component.

The first fractionation may be carried out in
such a way that sucrose and the second component are
enriched in the same fraction.

In accordance with a preferred embodiment of the
30   invention, sucrose and said second component are en-
riched in separate fractions in the first chromato-
graphic fractionation, and the sucrose fraction obtained
in the second fractionation is combined with the sucrose
fraction from the first fractionation, and sucrose is re-
35   covered   from   the   combined   sucrose   fraction   thus

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obtained.

In accordance with another preferred embodiment
of the invention, sucrose and said second component are
enriched in separate fractions in the first chromato-
5   graphic fractionation, and the second sucrose fraction
is returned to the feed solution for the first fraction-
ation. In this embodiment, sucrose is recovered from the
first sucrose fraction.

In accordance with another preferred embodiment
10   of the invention, a fraction enriched with sucrose and
the second dissolved component is recovered in the first
fractionation, and sucrose is recovered from the second
sucrose fraction and the second component from the frac-
tion enriched with said second dissolved component
15   obtained from the second fractionation. In this embodi-
ment, the sucrose fraction obtained is pure enough to
enable recovery of sucrose by methods commonly used in
the sugar industry. The fraction enriched with the
second dissolved component obtained from the second
20   fractionation can also be pure enough to enable recovery
of said component, e.g. betaine, by conventional tech-
niques.

Generally, the second dissolved component is re-
covered from the fraction obtained from the second frac-
25   tionation, which is enriched with the second dissolved
component. Part of the second dissolved component can be
recovered from a fraction enriched with said second dis-
solved component obtained from the first chromatographic
fractionation. Alternatively, said fraction enriched
30   with said second component obtained from the first chrom-
atographic fractionation is combined with the fraction
obtained in said second fractionation, which is enriched
with the second dissolved component. The term "second
dissolved component" refers to organic compounds com-
35   monly present in beet-derived solutions, such as beta-

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ine, inositol, raffinose, galactinol, or serine and other amino acids. The second chromatographic fractionation, i.e. fractionation of the fraction enriched with the second dissolved component which is obtained from
5   the first fractionation, may be performed by either a batch method or a SMB method.

The invention is particularly suitable for the recovery of sucrose and betaine from beet molasses. Therefore, the following description of the invention
10   specifically refers to the recovery of sucrose and betaine, but the invention is not so limited. Instead of, or in addition to betaine, any other dissolved organic substance may be similarly recovered by adjusting the process conditions and parameters to suit the separation in
15   question, which can be achieved easily by those skilled in the art.

With the method of the invention, the sucrose yield can be improved by up to about 10 per cent compared with the SMB methods presently employed in the
20   sugar industry. This improvement represents remarkable economic advantages in view of the large amounts of molasses used by the sugar industry for chromatographic separation. For example, in the United States, about 500,000 tonnes d.s. of molasses are currently used per
25   annum.

The purity of the sucrose fraction produced by the method of the invention is consistent with the goal of about 92% set for industrially practised SMB methods.

With regard to betaine, the method of the inven-
30   tion can achieve yields as high as about 95%, as contrasted with prior yields of about 30-70%, and a purity as high as about 95%, as contrasted with purities of about 25-70% (calculated on a dry solids basis) hitherto obtained.

35   The first chromatographic separation in the

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method of the invention may be carried out with prior
art SMB methods and apparatus known to be suitable for
the fractionation of molasses, such as those disclosed
in U.S. Patent 4,402,832 (continuous SMB method),
5   Finnish Patent 86,416, and international application WO
94/17213 (discussed above).

Also the further fractionation of the betaine
fraction produced in the first fractionation to yield a
second sucrose fraction and a second betaine fraction
10 may be carried out by known chromatographic separation
methods and apparatus, for example employing methods and
apparatus disclosed in the context of the batch method
in international application WO 81/02420 and in the con-
text of SMB methods in Finnish Patent 86,416 and inter-
15 national application WO 94/17213.

In the continuous SMB method, all flows (supply
of feed solution and eluant, recycling of liquid mix-
ture, and withdrawal of product fractions) are typically
continuous. The rates for these flows may be adjusted in
20 accordance with the separation goals (yield, purity,
capacity). There are normally 8 to 20 sectional packing
material beds that are combined into a single loop. The
feed and product withdrawal points are shifted cycli-
cally in the downstream direction in the packing mater-
25 ial bed. On account of the supply of eluant and feed
solution, the withdrawal of products, and the flow
through the packing material bed, a dry solids profile
is formed in the packing material bed. Constituents
having a lower migration rate in the packing bed are
30 concentrated in the back slope of the dry solids pro-
file, while ingredients having a higher migration rate
are concentrated in the front slope. The points of
introduction of the feed solution and eluant and the
withdrawal points of the product or products are shifted
35 gradually at substantially the same rate at which the

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dry solids profile moves in the packing material bed. The product or products are withdrawn substantially from the front and back slopes of the dry solids profile. The feed solution is introduced substantially at the point

5 where the composition of the cyclically moving dry solids profile is closest to the composition of the feed solution, and the eluant is introduced approximately at the point of minimum concentration of the dry solids profile. Part of the separated products are recycled on

10 account of the continuous cyclic flow, and only part of the dry solids profile is withdrawn from the packing material bed during one sequence.

The feed and withdrawal points are shifted cyclically by using feed and product valves located along

15 the packing material bed, typically at the upstream and downstream end of each sectional packing material bed. If it is desired to recover product fractions of very high purity, short phase times and multiple sectional packing material beds must be employed. The requisite

20 valves and feed and withdrawal equipment are part of the apparatus.

In the sequential SMB system, not all flows (supply of feed solution and eluant, recycling of liquid mixture, and withdrawal of products) are continuous. Yet

25 the shifting of the dry solids profile or profiles moving cyclically in the system is continuous. The flow rate and the volumes of the different feeds and product fractions may be adjusted in accordance with the separation goals (yield, purity, capacity).

30 During the feeding phase, a feed solution, and possibly also an eluant during a simultaneous eluting phase, is introduced into predetermined sectional packing material beds, and, simultaneously, one or more product fractions are withdrawn. During the eluting

35 phase, eluant is introduced into a predetermined sec-

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tional packing material bed or predetermined sectional
packing material beds and, during the feeding and
eluting phases, one or more product fractions are with-
drawn.

5   During the recycling phase, essentially no feed
solution or eluant is supplied to the sectional packing
material beds and essentially no products are withdrawn.
A forward flow is maintained in a fixed direction in a
system comprising at least two sectional packing mater-
10 ial beds, and the products are recovered during a multi-
step sequence comprising the above phases. A sectional
packing material bed may comprise one column, or it is
possible to pack several successive sectional packing
material beds into a single column.

15   During the feeding phase, feed solution is intro-
duced into a sectional packing material bed and a cor-
responding quantity of any product fraction is withdrawn
at a point which may be located either in the same sec-
tional packing material bed as the feed point (in which
20 case the other sectional packing material beds in the
system may be, for example, in the eluting or recycling
phase) or in a different sectional packing material bed
from that of the feed point, which bed is connected in
series (possibly through other sectional packing mater-
25 ial beds) with the sectional packing material bed into
which the feed is introduced. During the recycling
phase, the liquid in the sectional packing material
beds, along with its dry solids profile or profiles, is
recycled in a loop comprising one, two or several sect-
30 ional packing material beds. In the eluting phase,
eluant is introduced into the packing material bed and a
corresponding amount of product fraction(s) is (are)
withdrawn from the same or a downstream sectional pack-
ing material bed.

35   As stated previously, a detailed description of

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these sequential SMB methods applied to the recovery of sucrose and betaine from beet molasses is provided in Finnish Patent 86,416 and international application WO 94/17213; these processes may be employed in the method
5 of the present invention to carry out both the first and the second fractionation.

By moving the packing material bed counter-currently to the liquid flow direction of the dry solids profile, an actual moving bed system can be achieved. It
10 is self-evident that results very similar to those achieved with a simulated moving bed can be obtained with such an actual moving bed.

In the method of the invention, preferably a gel-type strong cation exchanger (e.g. "Dowex", "Finex" or
15 "Purolite") is employed as the packing material for the columns, and it is preferably in sodium and/or potassium form. The packing material is preferably equilibrated to the ionic form of the feed solution prior to the fractionation.

20 The dry solids content of the beet-derived sucrose-containing solution to be fed to the chromatographic separation is typically 20-80 g/100 g, preferably 40-70 g/100 g. The solution is heated to 40-95°C, preferably 65-85°C, prior to being supplied to the
25 separation process.

The elution phase employs mainly water and/or very dilute aqueous solutions (having a dry solids content less than 8% by weight, preferably less than 1% by weight). The eluant has a temperature of 40-95°C, pre-
30 ferably 65-85°C.

The dry solids content of the betaine fraction obtained from the first fractionation is adjusted prior to the second fractionation to about 25-50 g/100 g for batch separation or, typically, to 20-80 g/100 g, pre-
35 ferably 40-70 g/100 g, for SMB separation.

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Sucrose can be recovered from the sucrose frac-
tion by methods commonly used in the sugar industry,
such as by crystallization or as a syrup, or as liquid
sugar subsequent to purification. Betaine is at least
5   partly recovered from the betaine fraction obtained from
the second fractionation. This can be performed by crys-
tallization, for example, as described in international
application WO 81/02420, or said fraction can be used as
a concentrated betaine solution.

10   To optimize the sucrose and betaine yields and
purity, the pH of the feed solution may also be
adjusted. It is generally adjusted prior to the second
fractionation to the range 6.5-12, and preferably
between 9.5 and 11.5.

15   The following examples illustrate the method of
the invention in the context of fractionating beet molas-
ses to recover sucrose and betaine. These examples are
not to be construed as limiting the scope of the inven-
tion, but they are only illustrative of the special
20   embodiments of the invention.

Example 1

**Sequential SMB method; separation of sucrose and
betaine from molasses without further separation of
betaine fraction (reference example)**

25   A chromatographic apparatus as schematically
shown in Figure 1 was employed. The apparatus comprised
three columns 1-3 connected in series, fluid conduits 4-
7 connecting the columns, a molasses container 8, a
water/eluant container 9, a molasses feed conduit 10, an
30   eluant feed conduit 11, a recycle pump 12, a molasses
feed pump 13, an eluant feed pump 14, heat exchangers
15-17, product fraction withdrawal conduits 6, 18-20, 48
and 49, and valves 21-47. The apparatus further com-
prised flow and pressure regulators (not shown).

35   The columns were packed with a strong cation ex-

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changer resin Finex CS 11 GC™, manufacturer Finex Oy. The resin had a polystyrene/divinylbenzene backbone and was activated with sulphonic acid groups; the mean bead size (in Na⁺ form) was about 0.38 mm. The resin had a DVB
5   content of 5.5%. Prior to the test, the resin was regenerated to sodium form; during the fractionation it was equilibrated by cations from the feed solution.

     Test conditions:
10   Diameter of columns   0.2 m
     Total height of resin bed   10.5 m
     Temperature   80°C

     The feed solution was beet molasses wherefrom
15   calcium was precipitated by adding sodium carbonate (pH about 9); the calcium carbonate precipitate was removed by filtration.
     Fractionation was performed by a seven-step sequence that comprised the following steps:
20   Step 1: Feed solution 10 was introduced (feeding phase) into column 1 at a flow rate of 80 l/h, and a residue fraction was eluted from the downstream end of the same column 2 through conduit 48. Simultaneously, eluant was supplied (eluting phase) to column 2 through
25   valve 26 at a flow rate of 25 l/h, and a sucrose fraction was eluted from column 3 through conduit 6.
     Step 2: The liquid in the columns was recycled (recycling phase) in the loop formed by all columns at a rate of 120 l/h.
30   Step 3: Eluant was introduced into column 1 through valve 23 at a rate of 120 l/h and, simultaneously, a betaine fraction was eluted from column 3 through conduit 6.
     Step 4: Eluant 11 was introduced (eluting phase)
35   into column 1 through valve 23 at a flow rate of 120

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l/h, and a second residue fraction was eluted from the downstream end of column 2 through conduit 49. Simultaneously, eluant was supplied (eluting phase) to column 3 through valve 29 at a flow rate of 55 l/h, and a

5   second betaine fraction was eluted from the downstream end of the same column through conduit 6.

Step 5: Same as step 2.

Step 6: Eluant 11 was introduced into column 1 through valve 23 at a flow rate of 120 l/h, and a third

10 residue fraction was eluted from the downstream end of column 3 through conduit 6.

Step 7: Same as step 2.

After the sequence was carried to completion, the process control program was continued and it returned to

15 step 1. By repeating this sequence five to seven times, the system was equilibrated. The method proceeded in a state of equilibrium, and the progress of the separation process was monitored with a density meter, a meter for optical activity, and a conductivity meter, and the

20 separation was controlled by a microprocessor whereby precisely defined volumes and flow rates of feeds, recycled liquid and product fractions were controlled employing quantity/volume measuring means, valves and pumps.

25   In this method, a sucrose fraction from column 3, two betaine fractions from column 3, and one residue fraction from each column were withdrawn. The betaine fractions were combined, as were the residue fractions.

Analyses of the feed solution and the product

30 fractions withdrawn during one sequence after an equilibrium was reached are presented in Table 1, where the percentages of the different components are given as per cent by weight dry solids basis.

15

Table 1

	Dry solids g/100 g	Sucrose %	Betaine %
Feed solution	46.5	58.1	5.2
Sucrose fraction	25.8	92.1	0.8
Betaine fraction (combined)	4.2	18.1	55.6
Residue fraction (combined)	5.0	12.7	4.5

The sucrose yield into the sucrose fraction was 90.1% and the betaine yield into the combined betaine fraction 58.7%.

Example 2

Sequential SMB method; separation of sucrose and betaine from molasses, further separation of betaine fraction

The apparatus and test conditions described in Example 1 were employed. The procedure was also similar to that of Example 1, except that a higher purity, but lower yield, for sucrose and a lower purity, but higher yield, for betaine than in Example 1 were obtained in the first fractionation by adjusting the fraction volumes. Subsequent to evaporation, the resulting betaine fraction was subjected to re-fractionation by a similar sequential SMB method. The sucrose fraction obtained from the second fractionation was combined with the sucrose fraction from the first fractionation, and the residue fractions were likewise combined.

Analyses of the feed solutions and the product fractions withdrawn during one sequence after an equilibrium was reached are presented in Table 2, where the percentages of the different components are given as per cent by weight dry solids basis.

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Table 2

	Dry solids g/100g	Sucrose %	Betaine %
First fractionation			
Feed solution	46.5	58.1	5.2
Sucrose fraction	25.5	92.6	0.4
Betaine fraction	3.3	21.3	43.9
Residue fraction	4.8	11.7	0.9
Second fractionation			
Feed solution	55.0	21.3	43.9
Sucrose fraction	14.0	82.6	1.0
Betaine fraction	8.3	1.1	85.2
Residue fraction	4.1	11.2	2.2
Combined product fractions			
Sucrose fraction	24.7	92.2	0.4
Residue fraction	4.7	11.7	1.0

The sucrose yield from the first fractionation was 89.4% and the betaine yield was 89.9%. The total sucrose yield, calculated from the combined sucrose fraction, was 92.6% and the total betaine yield, calculated from the betaine fraction obtained from the second fractionation, was 88.2%. The second fractionation afforded remarkable improvement of the sucrose yield and betaine purity. In addition, the betaine yield improved significantly as compared with Example 1.

Example 3

The method described in Example 2 was essentially followed, but the effect of the pH of the feed solution for the second fractionation (which solution had been obtained from the betaine fraction from the first fractionation) was studied, performing the second fractionation in such a way that (a) the pH of the feed solution was not adjusted, and, hence, the pH was 10.2, (b) the

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pH of the feed solution was adjusted with hydrochloric acid to 9.5, and (c) the pH of the feed solution was adjusted with NaOH to 11.2.

5   Analyses of the feed solution for the second frac-tionation (i.e. further separation of the betaine frac-tion) and the product fractions withdrawn during one sequence after an equilibrium was reached are presented in Table 3, where the percentages of the different com-ponents are given as per cent by weight dry solids
10   basis.

Table 3

	Dry solids g/100 g	Sucrose %	Betaine %
Feed solution	43.0	32.5	24.8
(a) pH 10.2			
Sucrose fraction	16.6	84.6	0.1
Betaine fraction	6.2	0.4	89.3
(b) pH 9.5			
Sucrose fraction	17.9	81.1	0.1
Betaine fraction	6.2	0.4	88.0
(c) pH 11.2			
Sucrose fraction	15.4	82.5	0.1
Betaine fraction	6.1	0.1	90.4

25   The yields from the second fractionation in the above cases (a), (b) and (c) were as follows:

(a)   sucrose 57.3%, betaine 95.4%

(b)   sucrose 59.6%, betaine 96.8%

(c)   sucrose 51.9%, betaine 96.8%.

30   As will be seen from the results, the pH of the feed solution affects the purity and yield of sucrose and betaine. The pH may be adjusted in accordance with the economical optimum.

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Example 4

Continuous SMB method; separation of sucrose and by-product fraction from molasses (reference example)

The test apparatus comprised 14 columns connected
5   in series, each having a diameter of 0.2 m and each con-
taining a packing material bed having a height of
0.85 m. Figure 2 shows a schematic diagram of the test
apparatus.

The columns were packed with a polystyrene-based
10 cross-linked (5.5% DVB) strong cation exchanger having a
mean bead size of 0.32 mm. The packing material was equi-
librated with feed solution and was predominantly in
potassium and sodium form.

Water, as eluant, was introduced into the column
15 system at a flow rate of 83.5 l/h. Feed solution was
introduced through conduit 51 at each feed point at a
flow rate of 13.5 l/h for 150 seconds. The feed conduits
were rinsed with eluant (30 s, 13.5 l/h) subsequent to
the introduction of the feed solution. The flow rate of
20 the product fraction through valves 66-79 was adjusted
to 21 l/h, which produced a by-product flow rate of
76 l/h. The by-product fraction was withdrawn through a
spring-biased valve securing the desired pressure for
the system. An average recycle rate of 300 l/h was main-
25 tained. In practice, this rate varies according to the
change of the relative positions of the feed introduc-
tion and product withdrawal points along the recircula-
tion loop. The points of introduction of the feed solu-
tion and eluant and the withdrawal points of the product
30 fractions were shifted downstream one column each
successive step at intervals of 180 seconds.

Initially, the system was filled with a higher
feed flow rate and lower eluant flow rate. Once the sys-
tem was filled, the flow rate setpoints stated above
35 were used to run the system until an equilibrium had

19

been established.

Samples were taken at two-minute intervals via a
sampling valve placed in the recirculation loop. The con-
centration gradient shown in Figure 3 was drawn on the
5 basis of an analysis of the samples. In addition, the
feed solution and the product and by-product fractions
were analysed. The results are shown in Table 4, where
the percentages of the different components are given as
per cent by weight on a dry solids basis.
10

Table 4

	Feed solution	Product fraction	By-product fraction
Dry solids content, g/100 g	65.0	25.3	4.9
Sucrose, %	60.4	87.2	19.0
Betaine, %	5.5	4.5	7.0
Raffinose, %	2.1	0.9	4.0
Others, %	32.0	7.4	70.0
Flow rate, l/h	13.5	21.0	76.0
Sucrose yield into sucrose fraction 87.6			

Example 5

Continuous SMB method for separation of sucrose
25 and betaine from molasses and batch method for further
separation of betaine fraction

Molasses was fractionated by the continuous SMB
method, wherein the column system of Example 4 was modi-
fied in such a way that it was possible to withdraw
30 three product fractions: sucrose, betaine, and by-prod-
uct fractions. Figure 4 shows a schematic diagram of the
test apparatus. The flow rate of the sucrose fraction
was adjusted to 21 l/h and the flow rate of the betaine
fraction to 18 l/h. The feed rate of the eluant through

20

conduit 94 was 90.5 l/h, and the feed flow rate through conduit 95 was 13.5 l/h. Hence, the flow rate of the by-product fraction through conduit 96 was 65 l/h.

5   The betaine fraction was concentrated to a dry solids content of 55% and fed to a separation system comprising two columns connected in series. The columns had a diameter of 0.2 m, and the packing material bed in each column had a height of 0.85 m. The packing material was the same as in Example 4.

10   The betaine fraction was further fractionated using the batch method, supplying 2.6 l of feed solution (55% by weight on a dry solids basis) to the upstream end of the first column. The feed was repeatedly intro-duced at intervals of 60 minutes. Elution was performed

15   at a flow rate of 30 l/h. The following fractions were withdrawn from the bottom of the column:

Fraction 1:   By-product 8.6 l
Fraction 2:   Recycle fraction 2 l (introduced into the column prior to the actual feed)

20   Fraction 3:   Product solution 2.6 l
Fraction 4:   Recycle fraction 1.4 l (introduced into the column subsequent to the actual feed)
Fraction 5:   Betaine fraction 5.0 l
Fraction 6:   Elution recycling 10 l

25   With this procedure and column distribution, the betaine separation has a capacity more than twice the capacity of a single column system comprising 14 columns with respect to the betaine fraction produced.

The filling and equilibration of the column sys-
30   tem, sampling, and analyses of the samples were per-formed as above. The concentration gradient from the first continuous SMB separation is shown in Figure 5. The results are shown in Table 5, where the percentages of the different components are given as per cent by

35   weight on a dry solids basis.

Table 5

Fractionation of molasses, continuous SMB

	Dry solids content g/100 g	Sucrose %	Betaine %	Raffinose %	Others %	Flow rate l/h
Feed solution	65.0	60.4	5.5	2.1	32.0	13.5
Sucrose fraction I	25.2	87.6	4.5	0.9	7.0	21.0
Betaine fraction I	3.5	45.2	31.1	0.4	23.3	18.0
By-product fraction I	4.9	13.7	2.3	4.6	79.4	65.0

Sucrose yield into sucrose fraction 87.6%
Betaine yield into betaine fraction 37.0%

Fractionation of betaine fraction, batch method

	Dry solids content g/100 g	Sucrose %	Betaine %	Raffinose %	Others %	
Feed solution	55.0	45.2	31.1	0.4	23.3	
Sucrose fraction II	22.8	92.6	2.2	0.2	5.0	
Betaine fraction II	10.3	5.4	88.3	0.0	6.3	
By-product fraction II	4.5	18.0	3.2	1.2	77.6	

Sucrose yield into sucrose fraction 86.2%
Betaine yield into betaine fraction 94.5%

Combined sucrose and by-product fractions

	Dry solids content g/100 g	Sucrose %	Betaine %	Raffinose %	Others %	
Sucrose fraction I + II	25.1	87.8	4.4	0.9	6.9	
Betaine fraction II	10.3	5.4	88.3	0.0	6.3	
By-product fraction I + II	4.8	13.9	2.3	4.5	79.3	

Sucrose yield into sucrose fraction 91.8%
Betaine yield into betaine fraction 35.0%

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As can be seen from the results, the yield of
sucrose increased from 87.6% to 91.8% and the purity of
sucrose increased from 87.2% to 87.8%. With this simple
modification, betaine was recovered with a yield of
5   about 35% and a purity of 88.3%. The low betaine yield
is a result of the continuous SMB method in which the
feed flow was uninterrupted, and thus a considerable por-
tion of the betaine was lost in the sucrose fraction. By
increasing the eluant flow rate and increasing the flow
10   rate of the betaine fraction proportionately, the
betaine yield may increase up to about 50-60%.

        Example 6
        Sequential SMB method for separation of sucrose and
betaine from molasses and further separation of betaine
15   fraction
        The continuous SMB method disclosed in Example 4
was converted into a sequential method in such a way
that the columns of Example 4, referred to as sectional
packing material beds herein, were interconnected in
20   sequence to form a four-column system in which two col-
umns were formed by sectional packing material beds 1-3
and 4-6, and two columns by sectional packing material
beds 7-10 and 11-14. Thus, the system comprised two col-
umns having a total sectional packing material bed
25   height of 2.55 m each, and two columns having a total
sectional packing material bed height of 3.4 m each.
Figure 6 shows a schematic diagram of the apparatus.
        Fractionation was performed sequentially by the
following eight-step sequence:
30   Step 1: 15 l of feed solution was introduced into
sectional packing material bed 1 at a flow rate of 75
l/h, and a by-product fraction was withdrawn from sec-
tional packing material bed 10. 20 l of eluant was intro-
duced into sectional packing material bed 11 at a flow
35   rate of 100 l/h, and a sucrose fraction was withdrawn

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from sectional packing material bed 14.

Step 2: 8 l of liquid was recycled at a flow rate of 100 l/h in the loop formed by all columns.

Step 3: 12 l of eluant was introduced into sec-
5   tional packing material bed 1 at a flow rate of 120 l/h and a by-product fraction was withdrawn from sectional packing material bed 3. Simultaneously, 12 l of eluant was supplied to sectional packing material bed 4 at a flow rate of 120 l/h, and a betaine fraction was with-
10   drawn from sectional packing material bed 14.

Step 4: 14 l of eluant was introduced into sec-
tional packing material bed 1 at a flow rate of 120 l/h, and a betaine fraction was withdrawn from sectional pack-
ing material bed 14.

15   Step 5: 8 l of liquid was recycled at a flow rate of 100 l/h in the loop formed by all columns.

Step 6: 10 l of eluant was introduced into sec-
tional packing material bed 1 at a flow rate of 100 l/h, and a by-product fraction was withdrawn from sectional
20   packing material bed 14.

Step 7: 4 l of eluant was introduced into sectional packing material bed 1 at a flow rate of 120 l/h, and a by-product fraction was withdrawn from sectional packing material bed 14.

25   Step 8: 12 l of eluant was introduced into sec-
tional packing material bed 7. The profile was shifted by way of recirculation to sectional packing material bed 1, and a by-product fraction was withdrawn from sec-
tional packing material bed 6.

30   The betaine fraction was concentrated to a dry solids content of 55% and introduced into a separation system comprising three columns. Figure 7 shows a schem-
atic diagram of the apparatus. The columns had a dia-
meter of 0.2 m, and the packing material bed in each
35   column had a height of 0.85 m. The packing material was

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the same as in Example 4.

Fractionation was performed sequentially by the following eight-step sequence:

Step 1: 2 l of feed solution was introduced into
5   column 1 at a flow rate of 60 l/h, and a by-product fraction was withdrawn from column 2. 2.7 l of eluant was supplied to column 3 at a flow rate of 80 l/h, and a sucrose fraction was withdrawn from column 3.

Step 2: 1.5 l of feed solution was supplied to col
10   umn 1 at a flow rate of 60 l/h, and a sucrose fraction was withdrawn from column 3.

Step 3: 1.5 l of liquid was recycled at a flow rate of 60 l/h in the loop formed by all columns.

Step 4: 3 l of eluant was introduced into column 1
15   at a flow rate of 60 l/h, and a betaine fraction was withdrawn from column 3.

Step 5: 1.8 l of eluant was introduced into column 1 at a flow rate of 54 l/h, and a by-product fraction was withdrawn from column 1. Simultaneously, 4 l of elu
20   ant was supplied to column 2 at a flow rate of 120 l/h, and a betaine fraction was withdrawn from column 3.

Step 6: 3 l of liquid was recycled at a flow rate of 60 l/h in the loop formed by all columns.

Step 7: 1.5 l of eluant was introduced into column
25   1 at a flow rate of 60 l/h, and a by-product fraction was withdrawn from column 3.

Step 8: 3 l of liquid was recycled at a flow rate of 60 l/h in the loop formed by all columns.

With this procedure, the betaine separation has
30   more than double the capacity of the first separation stage with respect to the amount of the betaine fraction produced. Thus, it was not attempted in this test to optimize the sequence with respect to capacity and energy consumption, but good yields and purities were
35   pursued. This resulted in low fraction concentrations.

25

It is obvious to those skilled in the art that, in actual industrial practice, optimization is realized on an economic basis, thus the optimum values may be rather different from the values disclosed herein.

5   The filling and equilibration of the column system, sampling, and analyses of the samples were performed similarly as in Example 4. The concentration gradient from the output of sectional packing material bed 14 in the first continuous SMB separation is shown in Figure 8.
10   The results are shown in Table 6, where the percentages of the different components are given as per cent by weight on a dry solids basis.

Table 6

Fractionation of molasses, sequential SMB					
	Dry solids content g/100 g	Sucrose %	Betaine %	Raffinose %	Others %
Feed solution	55.0	60.4	5.5	2.1	32.0
Sucrose fraction I	24.3	92.3	0.9	1.2	5.6
Betaine fraction I	3.9	44.9	45.5	0.7	8.9
By-product fraction I	5.9	14.1	0.6	4.0	81.3

Sucrose yield into sucrose fraction 84.1%
Betaine yield into betaine fraction 87.3%

Fractionation of betaine fraction, sequential SMB					
Feed solution	55.0	44.9	45.5	0.7	8.9
Sucrose fraction II	22.5	91.7	5.3	0.5	2.5
Betaine fraction II	16.0	7.4	88.9	0.0	3.7
By-product fraction II	3.0	25.3	1.0	5.5	68.2

Sucrose yield into sucrose fraction 87.0%
Betaine yield into betaine fraction 94.8%

Combined sucrose and by-product fractions					
Sucrose fraction I + II	24.2	92.3	1.2	1.1	5.4
Betaine fraction II	16.0	7.4	88.9	0.0	3.7
By-product fraction I + II	5.7	14.4	0.6	4.0	81.0

Sucrose yield into sucrose fraction 91.0%
Betaine yield into betaine fraction 82.8%

As can be seen from Figure 8, significantly better separation of betaine from sucrose is achieved compared to the fully continuous method of Example 5. Table 6 shows that with substantially similar column
5   loads, the sequential method also yields a considerably higher purity of 92.3%, for the sucrose fraction than the 87.2-87.8% for the fully continuous method. Double separation permits the first fractionation to be performed with a relatively low sucrose yield, e.g. 84.1%,
10   thus realizing the need for a high separation capacity and low evaporation. Double separation increases the sucrose yield to 91.0%. The betaine yield may easily be increased to 82.8%, and with a higher eluant quantity and column capacity, the betaine yield may exceed 90%.

15   **Example 7**

Continuous SMB method for the separation of by-product and a combined sucrose and betaine fraction from molasses followed by a continuous SMB method for the separation of sucrose fraction and betaine fraction from
20   the combined sucrose and betaine fraction

The test apparatus and resin described in Example 4 were used for the experiment.

Water, as eluant, was introduced into the column system at a flow rate of 144.6 1/h. Feed solution was
25   introduced through conduit 51 at each point at a flow rate of 23 1/h for 165 seconds. The feed conduits were rinsed with eluant (15 s, 22.9 1/h) subsequent to the introduction of the feed solution. The flow rate of the product fraction through valves 66-79 was adjusted to
30   33.9 1/h, which produced a by-product flow of 133.7 1/h. The by-product was withdrawn through a spring-biased valve securing the desired pressure for the system. An average recycle rate of 290 1/h was maintained. In practice, this rate varies according to the change of the
35   relative positions of the feed introduction and product

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withdrawal points along the recirculation loop. The
points of introduction of the feed solution and eluant
and the withdrawal points of the product fractions were
shifted downstream one column each successive step at
5   intervals of 180 seconds.

As stated in Example 4, the system was allowed to
reach an equilibrium before sampling.

When the recycling rate is lowered in relation to
the feed and product flow rates, more betaine will end
10   up in the product fraction than in Example 4. The
sucrose purity of the product fraction will be lower
(85.6% instead of 87.2%). However, the separation capa-
city will be significantly higher.

The product fraction from this separation, con-
15   taining most of the sucrose and betaine, was collected
and used as a feed solution in a similar continuous SMB
system. No evaporation was needed, the product fraction
was used as such.

Water, as eluant, was introduced into the column
20   system at a flow rate of 42.4 l/h. Feed solution was
introduced through conduit 51 at each point at a flow
rate of 34.9 l/h for 300 seconds. The feed conduits were
rinsed with eluant (10 s, 34.9 l/h) subsequent to the
introduction of the feed solution. The flow rate of the
25   betaine fraction through valves 66-79 was adjusted to
37.9 l/h, which produced a sucrose fraction flow of 39.4
l/h. The by-product was withdrawn through a spring-
biased valve securing the desired pressure for the sys-
tem. An average recycle rate of 170 l/h was maintained.
30   In practice, this rate varies according to the change of
the relative positions of the feed introduction and
product withdrawal points along the recirculation loop.
The points of introduction of the feed solution and elu-
ant and the withdrawal points of the product fractions
35   were shifted downstream one column each successive step

29

at intervals of 310 seconds.

The results of this test are shown in Table 7. It
is to be seen that the results are clearly better than
when it is attempted to obtain three product fractions
5   from a continuous SMB system, as set forth in Example 5.
The final betaine purity is lower (52.5% instead of
88.3%), but the overall recovery of betaine is much
better (63.7% instead of 35%) and, more importantly, the
purity of the sucrose fraction is significantly higher
10   (93.6% instead of 87.8%). The final sugar product can be
recovered by crystallization of this sucrose fraction
and, owing to the high purity, the yield from the crys-
tallization will be significantly higher. It is also pos-
sible to purify this high-quality sucrose fraction by
15   ion exchange and adsorption techniques into a colourless
or nearly colourless liquid sugar product or syrup.

Table 7

Fractionation of molasses, continuous SMB					
	Dry solids content (DS) g/100 g	Sucrose % of DS	Betaine % of DS	Raffinose % of DS	Others % of DS	Flow rate l/h
Feed solution	65.0	60.4	5.5	2.1	32.0	23.0
Product fraction	30.7	85.6	6.0	0.8	7.5	33.9
By-product fraction	4.7	13.8	4.6	4.4	77.2	133.7

Sucrose yield into product fraction 92.0%
Betaine recovery into product fraction 70.8%

Fractionation of product fraction, continuous SMB					
Product fraction	30.7	85.6	6.0	0.8	7.5	34.9
Sucrose fraction	24.1	93.6	0.7	0.8	5.0	39.9
Betaine fraction	3.2	16.6	52.5	1.6	29.2	37.4

Sucrose yield into sucrose fraction 98.0%
Betaine yield into betaine fraction 90.0%

Overall sucrose yield into sucrose fraction 90.2%
Overall betaine yield into betaine fraction 63.7%

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Claims:

1. A method for separating sucrose and addi-
tionally a second dissolved component from a beet-
derived sucrose-containing solution,   c h a r a c -
t e r i z e d   in that the solution is subjected to a
first fractionation by a chromatographic simulated
moving bed method to yield a sucrose-enriched fraction
and a fraction enriched with the second dissolved com-
ponent or a fraction enriched with sucrose and the
second dissolved component, and the resulting fraction
enriched with the second component or with sucrose and
the second dissolved component is subjected to a second
chromatographic fractionation, to yield a second suc-
rose-enriched fraction and a separate fraction enriched
with the second dissolved component.

2. A method as claimed in claim 1,   c h a r a c -
t e r i z e d   in that a fraction enriched with sucrose
and, separately therefrom, a fraction enriched with the
second dissolved component are recovered in the first
fractionation.

3. A method as claimed in claim 2,   c h a r a c -
t e r i z e d   in that the second sucrose-enriched frac-
tion is combined with the sucrose fraction from the
first chromatographic fractionation, and sucrose is re-
covered from the combined sucrose fraction thus
obtained.

4. A method as claimed in claim 2,   c h a r a c -
t e r i z e d   in that the second sucrose-enriched frac-
tion is returned to the feed solution for the first
chromatographic fractionation, and sucrose is recovered
from the sucrose-enriched fraction obtained from the
first fractionation.

5. A method as claimed in claim 1,   c h a r a c -
t e r i z e d   in that a fraction enriched with sucrose

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and the second dissolved component are recovered in the first fractionation.

6. A method as claimed in claim 5, c h a r a c - t e r i z e d in that sucrose is recovered from the
5   second sucrose-enriched fraction.

7. A method as claimed in any one of claims 1-6, c h a r a c t e r i z e d in that the second dissolved component is recovered at least partly from the fraction enriched with said second dissolved component and
10   obtained from the second fractionation.

8. A method as claimed in any one of claims 1-7, c h a r a c t e r i z e d in that the second dissolved component is selected from betaine, inositol, raffinose, galactinol, and serine and other amino acids.
15   9. A method as claimed in claim 8, c h a r a c - t e r i z e d in that the second dissolved component is betaine.

10. A method as claimed in any one of claims 1-9, c h a r a c t e r i z e d in that the simulated moving
20   bed method is a continuous simulated moving bed method.

11. A method as claimed in any one of claims 1-9, c h a r a c t e r i z e d in that the simulated moving bed method is a sequential simulated moving bed method.

12. A method as claimed in any one of claims 1-
25   11, c h a r a c t e r i z e d in that the second frac- tionation is performed by a batch method.

13. A method as claimed in any one of claims 1- 11, c h a r a c t e r i z e d in that the second frac- tionation is performed by a continuous simulated moving
30   bed method.

14. A method as claimed in any one of claims 1- 11, c h a r a c t e r i z e d in that the second frac- tionation is performed by a sequential simulated moving bed method.
35   15. A method as claimed in any one of claims 1-

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14, c h a r a c t e r i z e d in that the beet-derived
sucrose-containing solution is beet molasses.

16. A method as claimed in any one of claims 1-
15, c h a r a c t e r i z e d in that the chromato-
graphic fractionation is performed with a strong cation
exchanger.

17. A method as claimed in claim 15, c h a r -
a c t e r i z e d   in that the cation exchanger is a
polystyrene-based cation exchanger cross-linked with
divinylbenzene and having a divinylbenzene content of 4-
8%.

18. A method as claimed in claim 16 or 17,
c h a r a c t e r i z e d   in that the cation exchanger
is predominantly in sodium and/or potassium form.

19. A method as claimed in any one of claims 1-
18, c h a r a c t e r i z e d   in that the dry solids
content of the solution fed to the second fractionation
is adjusted.

20. A method as claimed in any one of claims 1-
19, c h a r a c t e r i z e d   in that the pH of the
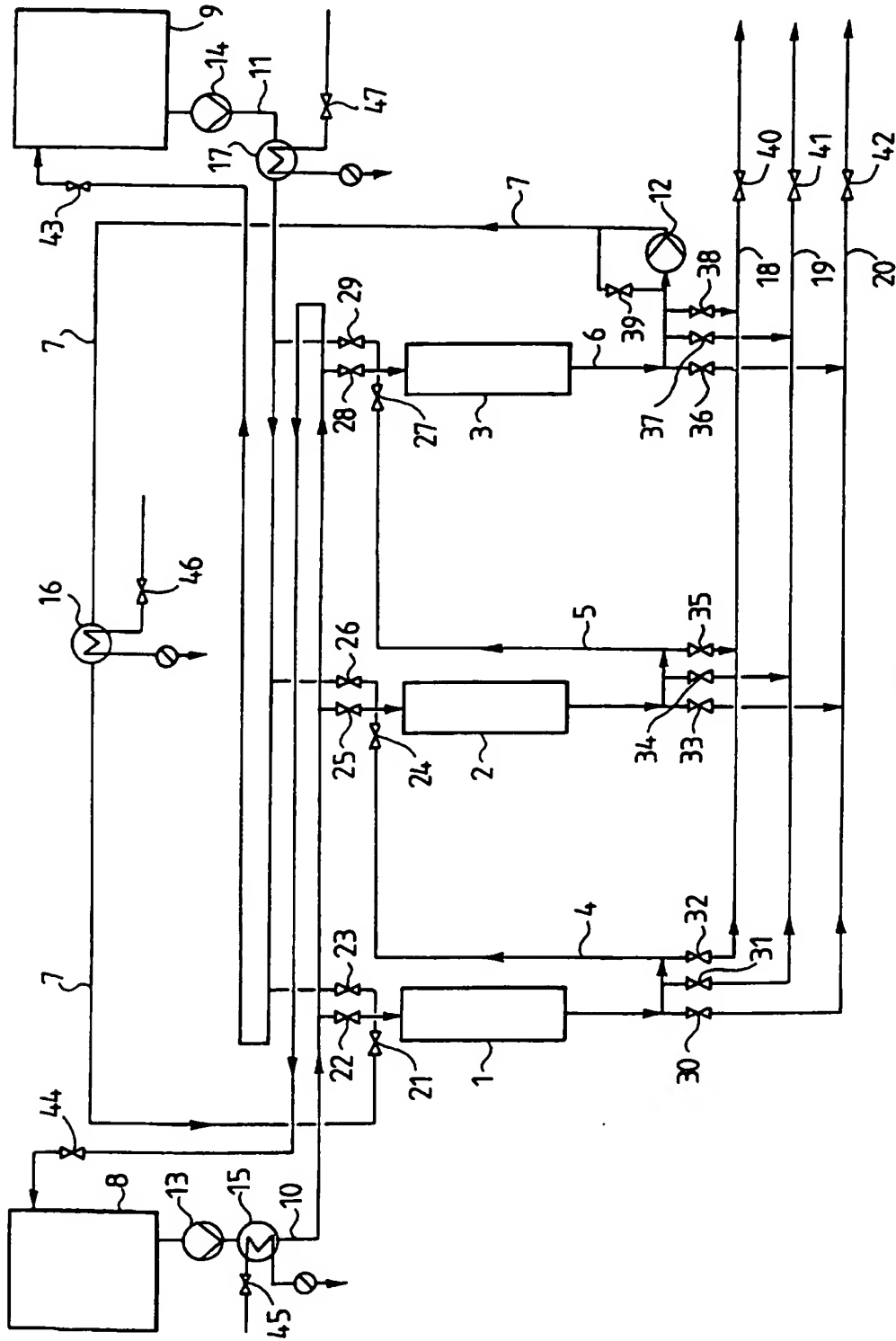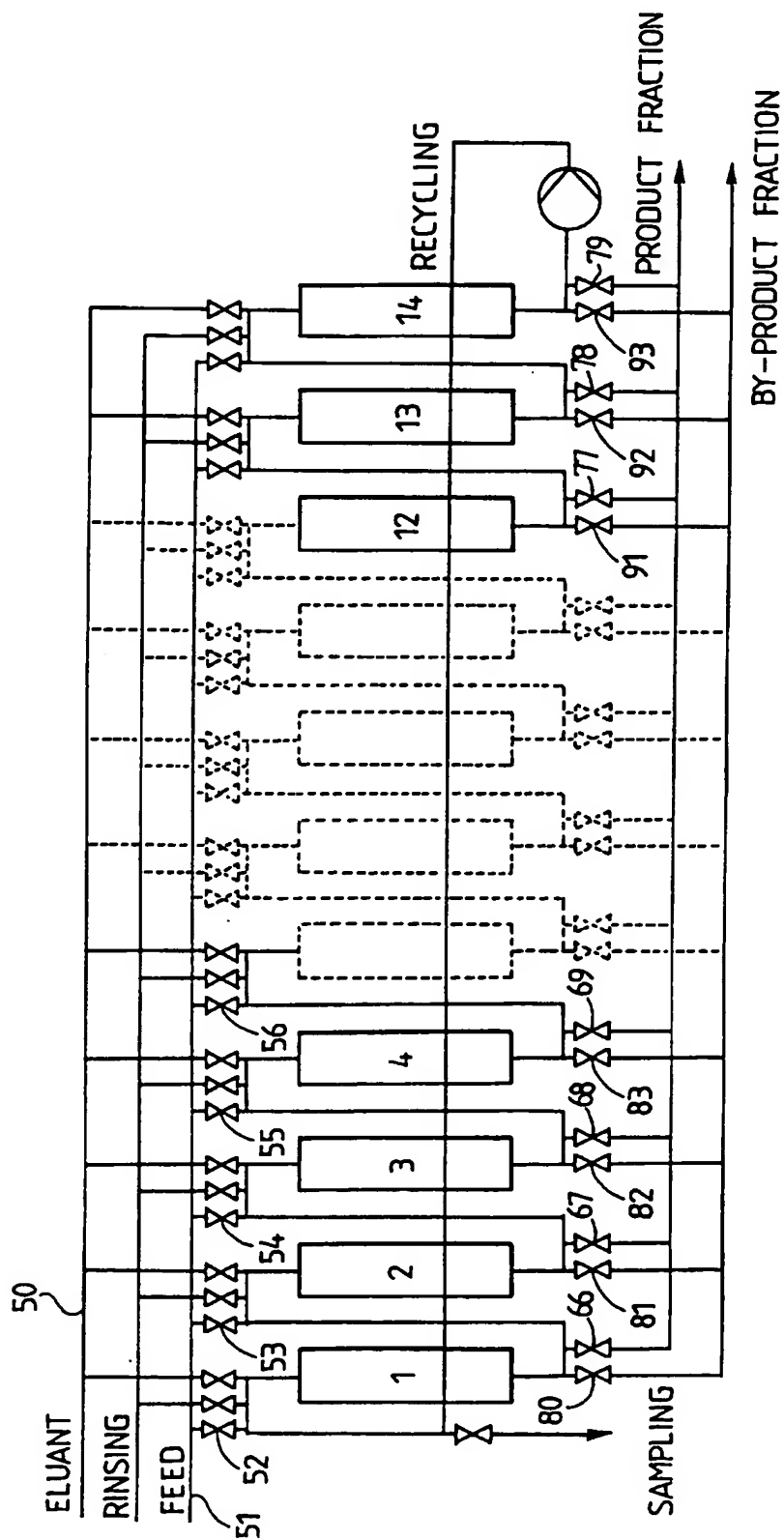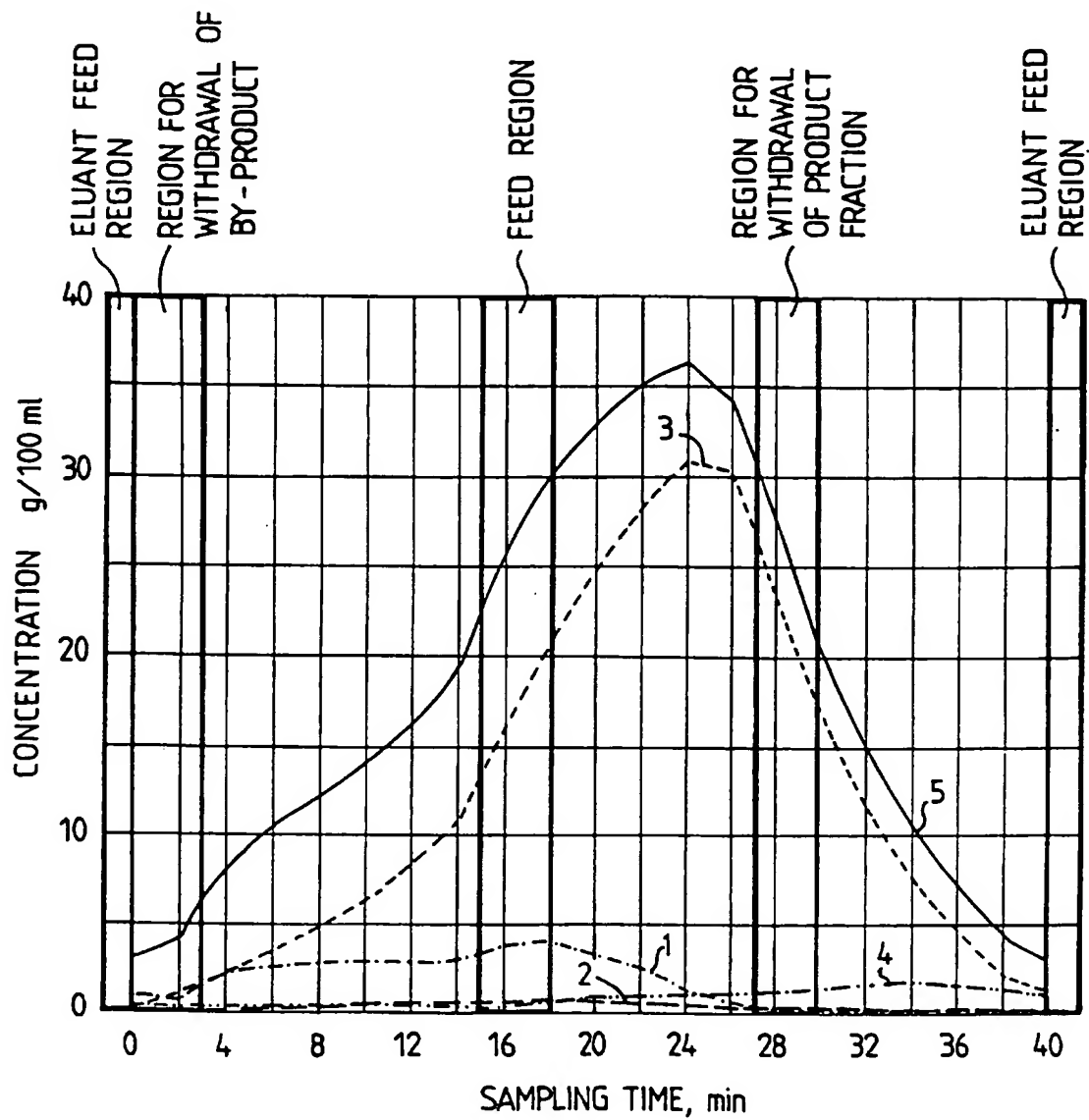solution fed to the second fractionation is adjusted to
the range 6.5-12.

FIG. 1

FIG. 2

1   SALTS (HPLC)
2   RAFFINOSE
3   SUCROSE
4   BETAINE
5   CONCENTRATION

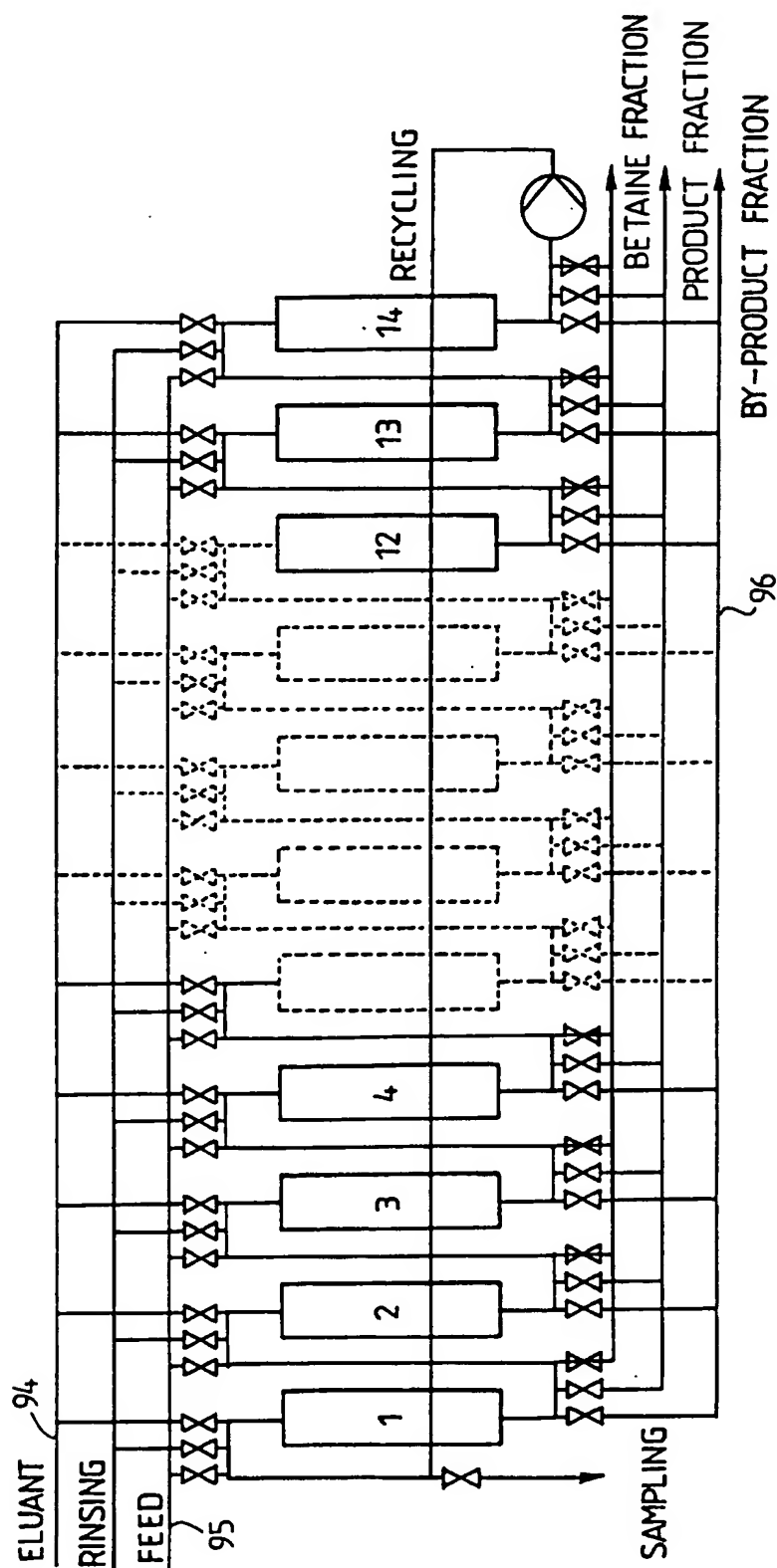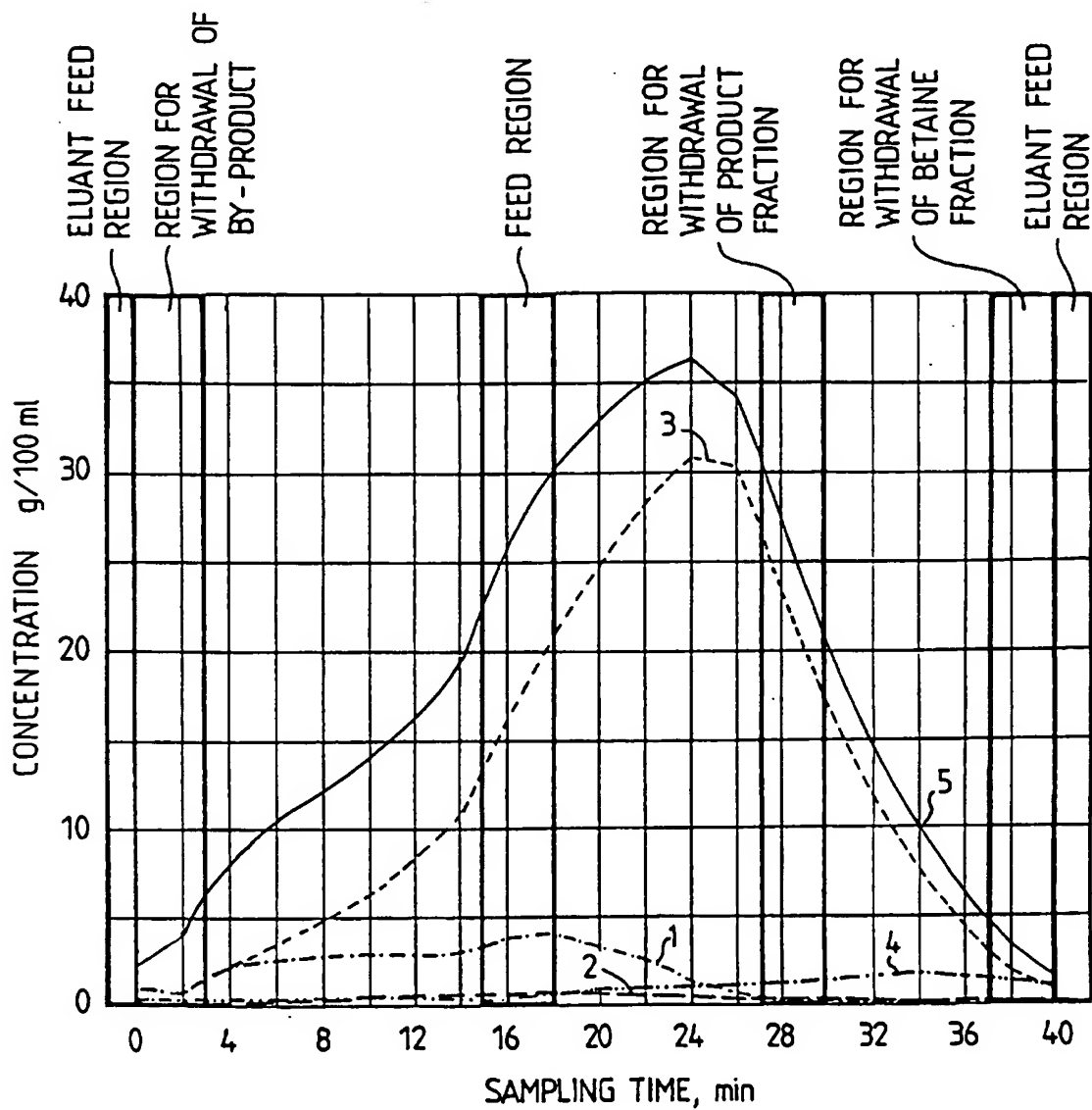FIG. 3

FIG. 4

FIG. 5

1 SALTS (HPLC)
2 RAFFINOSE
3 SUCROSE
4 BETAINE
5 CONCENTRATION

FIG. 6

FIG. 7

1   SALTS (HPLC)
2   RAFFINOSE
3   SUCROSE
4   BETAINE
5   CONCENTRATION

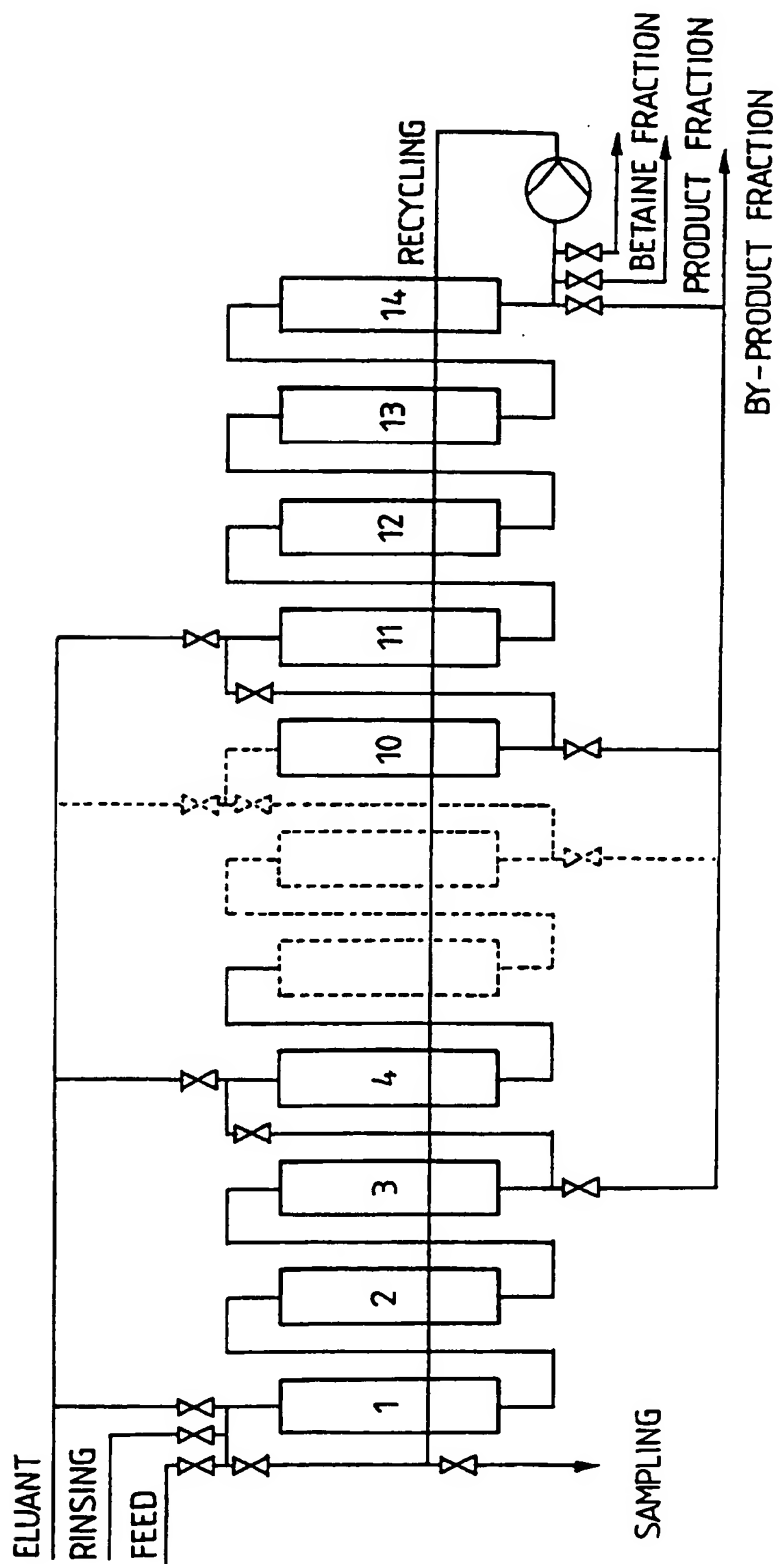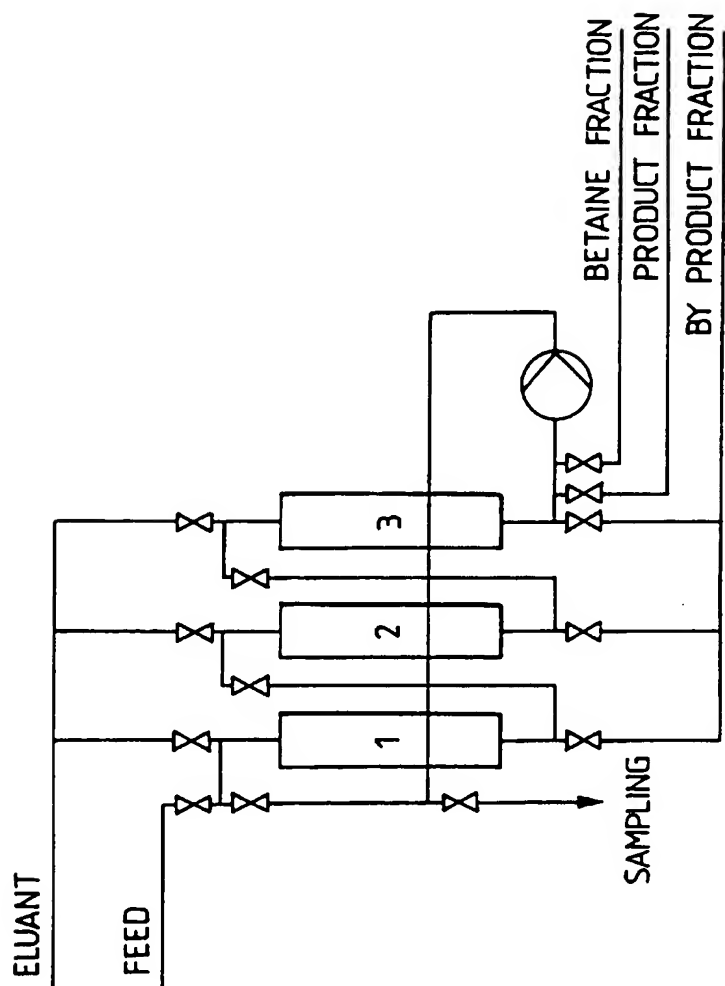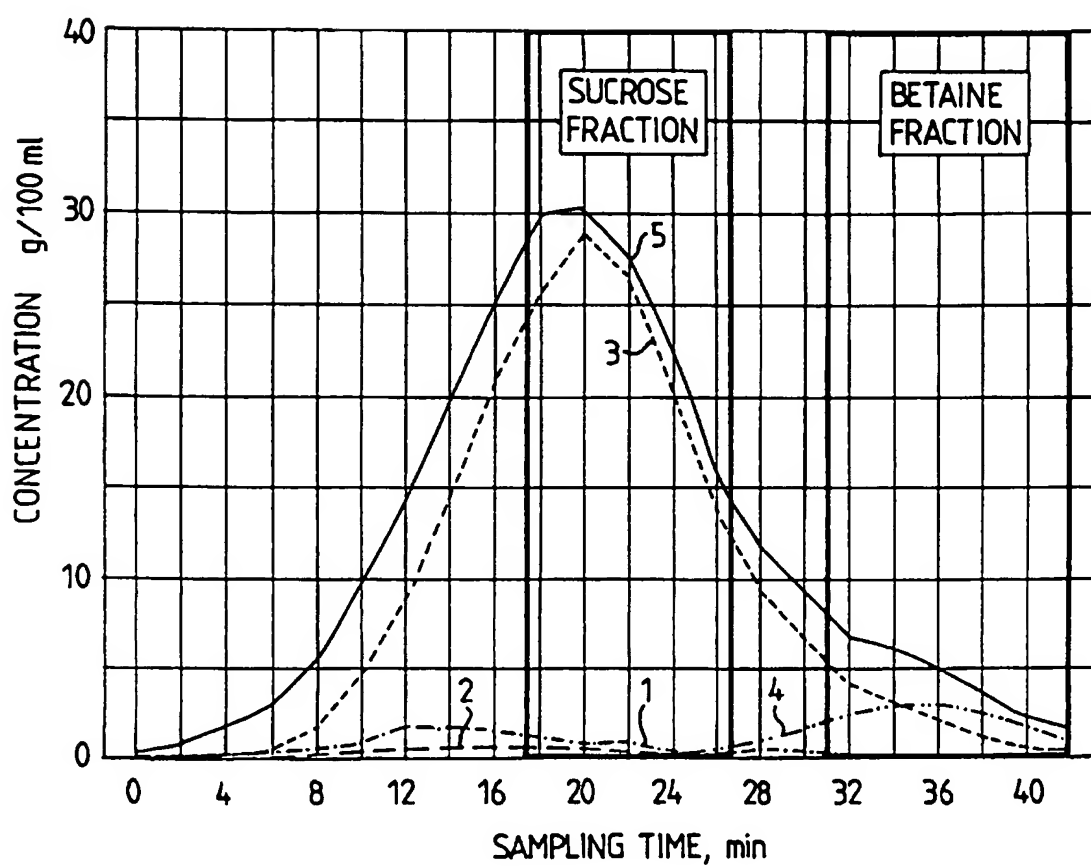FIG. 8

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C13D 3/14, C13J 1/06
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C13D, C13J, B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, IFIPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 9417213 A1 (H. HEIKKILÄ ET AL), 4 August 1994 (04.08.94) --	1-20
Y	US 5217957 A (H. HEIKKILÄ ET AL), 7 July 1992 (07.07.92) --	1-20
A	WO 8102420 A1 (H. HEIKKILÄ ET AL), 3 Sept 1981 (03.09.81) --	1-20
A	EP 0101304 A2 (C.G. GERHOLD), 22 February 1984 (22.02.84) --	1-20

[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 January 1996	12 -02- 1996

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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00538

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2985589 A (D.B. BROUGHTON ET AL), 23 May 1961 (23.05.61) --	1-20
A	US 5102553 A (M.M. KEARNEY ET AL), 7 April 1992 (07.04.92) -- --------	1-20

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US-A- 5217957	07/07/92	AU-A-	2543992	16/03/93
		WO-A-	9303721	04/03/93
		ZA-A-	9206245	21/02/94
WO-A1- 8102420	03/09/81	AT-E,T-	11132	15/01/85
		BE-A,A-	887652	15/06/81
		EP-A,B-	0054544	30/06/82
		SE-T3-	0054544	
		US-A-	4359430	16/11/82
EP-A2- 0101304	22/02/84	SE-T3-	0101304	
		AU-B,B-	565872	01/10/87
		AU-A-	1763383	16/02/84
		CA-A-	1190724	23/07/85
		JP-C-	1667193	29/05/92
		JP-B-	3025201	05/04/91
		JP-A-	59080306	09/05/84
		US-A-	4402832	06/09/83
		US-A-	4478721	23/10/84
US-A- 2985589	23/05/61	NONE		
US-A- 5102553	07/04/92	AU-A-	4815690	10/07/90
		CA-A-	2005702	16/06/90
		EP-A,A-	0448633	02/10/91
		JP-T-	4502276	23/04/92
		JP-B-	7034010	12/04/95
		US-A-	4990259	05/02/91
		WO-A-	9006796	28/06/90
		AU-A-	6908291	18/07/91
		WO-A-	9108815	27/06/91